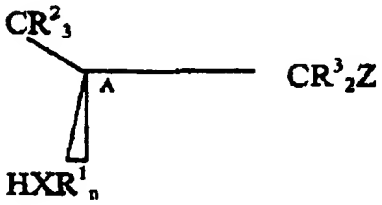
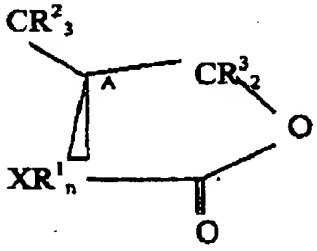
CLAIMS

1. Process for the preparation of enantiomerically pure compounds of formula I:

(I) 

comprising contacting a compound of formula II:

(II) 

with a source of hydrogen at ambient temperature and elevated pressure in the range 1 – 10 atm for a period *which is other than 2 hours or less (proviso taking basis from D3); alternatively for a period of 43 hours (taking basis from Examples); alternatively for a period in the range 43 to 93 hours (taking basis from examples)* in the presence of a hydrogenation catalyst which is homogeneous or heterogeneous and comprises a metal selected from the transition metals of Group VIII of the Periodic Table of the Elements and a catalytic support; or

with a source of fluorine as a fluorination agent which comprises gaseous or liquid phase HF and a carrier, at temperature in the range 0 – 20C and ambient pressure for a period of 24 hours

wherein A is *an enantiomerically pure* centre *CH*; Z is hydrogen or *fluoro*

X is selected from oxygen, sulphur and nitrogen and n is selected from 0 and 1 and is equal to the valence of X less 2; and R^1 to R^3 are as defined below

and wherein each R^1 is independently selected from hydrogen or from straight chain or branched, saturated or unsaturated C_{1-8} hydrocarbon optionally substituted by one or more hydroxy, halo, aryl, cyclo C_{1-8} alkyl;

each R^3 is independently selected from hydrogen or halo; and straight and branched chain, saturated and unsaturated C_{1-4} alkyl, alkenyl and alkynyl and aryl;
each optionally substituted by hydroxy, halo, saturated or unsaturated C_{1-4} alkyl, alkenyl or alkynyl, aryl, cyclo C_{1-6} alkyl, carbonyl, carboxyl, amino, amido;

each R^2 is independently selected from hydrogen, straight chain and branched, saturated and unsaturated C_{1-8} alkyl, optionally substituted by hydroxy, halo, aryl, cyclo C_{1-6} alkyl, carbonyl, carboxyl, amino, amido.

2. Process as claimed in Claim 1 wherein X is nitrogen whereby n is 1.

3. Process as claimed in any one of Claims 1 and 2 wherein R^3 is selected from ethenyl, ethynyl and optionally substituted phenyl.

4. Process as claimed in any one of Claims 1-3 wherein at least one and preferably both of R^3 are aryl.

5. Process as claimed in any one of Claims 1-4 wherein R^2 is selected from optionally hydroxy, halo or alkoxy substituted branched and straight chain C_{1-6} alkyl, including methyl, ethyl, i-propyl, i-butyl, t-butyl; and aryl including phenyl and benzyl.

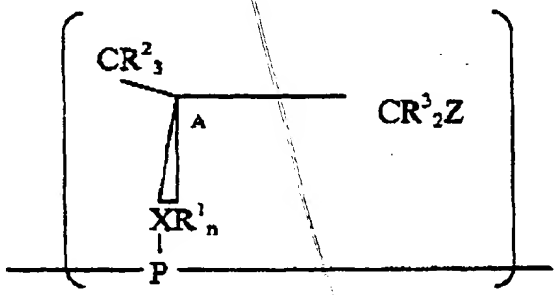
6. Process as claimed in any one Claims 1 to 5 wherein X is nitrogen wherein n is 1 and R^1 is H, i.e. the compound is a primary amine.

7. Process as claimed in any one of Claims 1-6 wherein a catalyst comprises Pd with C as catalytic support.

8. Process as claimed in any of Claims 1-7 wherein a fluorination agent is liquid phase HF-pyridine.

9 [13,14[16,17]]. *Process for preparation of a compound of the formula I as hereinbefore defined in any of Claims 1 to 8 which is a process for the* preparation of enantiomerically pure enantiomerically pure polymer comprising a repeating unit of the formula Ii:

(Ii)

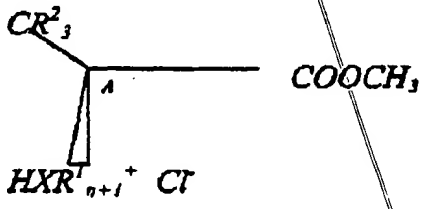


wherein P is derived from a polymerisable monomer or oligomer and X, R^1, R^2, R^3, Z and A are as hereinbefore defined in any of Claims 1 to 6; and

wherein a polymerisable monomer is selected from the group consisting of: an epoxy resin; an addition-polymerisation resin; a formaldehyde condensate resin; a cyanate resin; and an isocyanate resin; polyaromatics; monomers of natural polymers including carbohydrates, polypeptides and proteins including starch, celluloses, collagen, gelatin, dextrans, alginates, chitin and chitosan; and monomers of biodegradeable and/or biocompatible polymers including poly(lactic acid), poly(glycolic acid), polycaprolactone, polyorthoesters, polyanhydrides, polyaminoacids and azo polymers; and mixtures thereof.

10 [17,18[20,21]]. *Process for preparation of enantiomerically pure compounds of formula I as hereinbefore defined in any of Claims 1 to 8 which is a process for the* preparation of a library of compounds comprising:

reacting one or more compounds of formula IV

(IV) 

Wherein *R^1, R^2 and A are as hereinbefore defined in any of Claims 1 to 6*

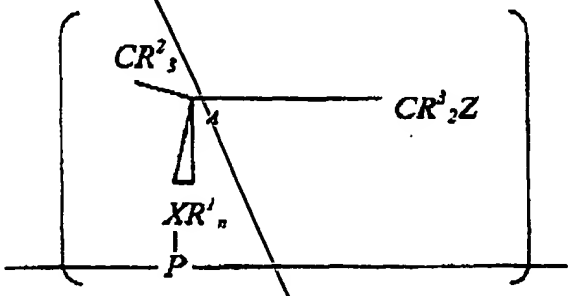
with a plurality of compounds of formula V R^2MgBr, and converting via compounds of formula II as hereinbefore defined *in Claim 1 to 6* to compounds of formula I as hereinbefore defined *in any of Claims 1 to 6*; and

optionally labelling the support or vessel with means to identify the synthetic history of the supported or contained compound.

11 [12]. *Enantiomerically pure* compound of the formula I as hereinbefore defined in any of Claims 1 to 6 wherein A, Z and R^1 to R^3 are as hereinbefore defined, X is N and n is 1.

12 [15[18]]. *Enantiomerically pure polymer comprising a repeating unit of the formula Ii:*

(Ii)



wherein *P is derived from a polymerisable monomer or oligomer selected from the group consisting of: an epoxy resin; an addition-polymerisation resin; a formaldehyde condensate resin; a cyanate resin; and an isocyanate resin; polyaromatics; monomers of natural polymers including carbohydrates, polypeptides and proteins including starch, celluloses, collagen, gelatin, dextrans, alginates, chitin and chitosan; and monomers of biodegradeable and/or biocompatible polymers including poly(lactic acid), poly(glycolic acid), polycaprolactone, polyorthoesters; and*

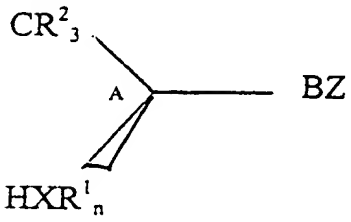
X, R^1, R^2, R^3, Z and A are as hereinbefore defined in any of Claims 1 to 6.

13 [19 [22]]. Library of enantiomerically pure compounds of formula I as hereinbefore defined *in Claim 11*.

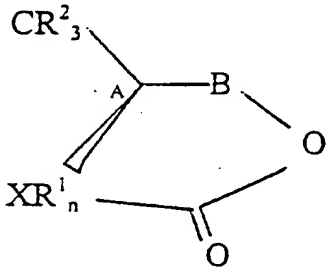
14 [20 [23]]. Pharmaceutical, veterinary product or agrochemical composition comprising an enantiomerically pure compound of formula I, Ii or Iii as hereinbefore defined *in any of Claims 11 - 13* with suitable diluents, adjuvants, carriers.

CLAIMS

1. Process for the preparation of chiral compounds of formula I:

(I) 

comprising contacting a compound of formula II:

(II) 

with a source of hydrogen or halide;

wherein A is a chiral centre;

X is selected from oxygen, sulphur and nitrogen;

n is selected from 0 and 1 and is equal to the valence of X less 2;

Each R^1 is independently selected from hydrogen, straight chain and branched, saturated and unsaturated C_{1-8} hydrocarbon optionally substituted by one or more hydroxy, halo, aryl, cyclo C_{1-8} alkyl and the like;

B is a fragment CR^3_2 wherein each R^3 is independently selected from hydrogen, halo, azides and cyanides; straight and branched chain, saturated and unsaturated C_{1-4} alkyl, alkenyl and alkynyl and aryl, each optionally substituted by hydroxy, halo, saturated

or unsaturated C_{1-4} alkyl, alkenyl or alkynyl, aryl, cyclo C_{1-6} alkyl, carbonyl, carboxyl, amino, amido, (thio)ether, haloalkyl, silylalkyl and the like;

Z is hydrogen or halogen;

each R^2 is independently selected from hydrogen, straight chain and branched, saturated and unsaturated C_{1-8} alkyl, optionally substituted by hydroxy, halo, aryl, cyclo C_{1-6} alkyl, carbonyl, carboxyl, amino, amido, (thio)ether and the like; and

one of R^1 and one of R^2 together may form an alkylene group as part of a heterocyclic ring;

with the proviso that when X is nitrogen, n is 1, one of R^1 and two of R^2 are hydrogen, BZ is $CHPh_2$, the other R^1 and R^2 do not form together a five membered heterocyclic (pyrrolidone) ring.

2. Process as claimed in Claim 1 wherein X is nitrogen whereby n is 1.

3. Process as claimed in any one of Claims 1 and 2 wherein B is a fragment CR^3_2 wherein R^3 is selected from ethenyl, propenyl ethynyl and propynyl, optionally substituted phenyl.

4. Process as claimed in any one of Claims 1-3 wherein B is a group as hereinbefore defined wherein at least one and preferably both of R^3 are aryl.

5. Process as claimed in any one of Claims 1-4 wherein Z is selected from hydrogen, chloro and fluoro.

6. Process as claimed in Claim 5 wherein R^2 is selected from optionally hydroxy, halo, alkoxy substituted branched and straight chain C_{1-6} alkyl, including methyl, ethyl, i-propyl, i-butyl, t-butyl; and aryl including phenyl and benzyl.

7. Process as claimed in any one of Claims 1-6 wherein X is nitrogen wherein n is 1 and R^1 does not form a cyclic ring with one of R^2 or R^1 is H, and R^2 is other than H, i.e. the compound is a primary amine.

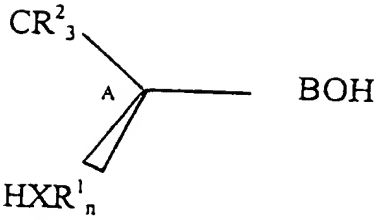
8. Process as claimed in any of Claims 1-7 conducted in the presence of a catalyst which is homogeneous or heterogeneous or of an agent which is gaseous or liquid.

9. Process as claimed in Claim 8 wherein the catalyst is a hydrogenation catalyst comprising a metal selected from the transition metals of Group VIII of the Periodic Table of the Elements optionally in the presence of or including additional catalytic components or catalytic supports such as C.

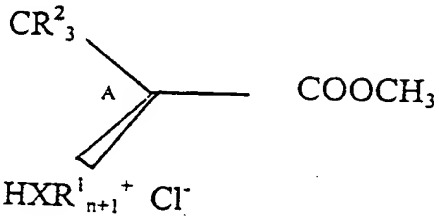
10. Process as claimed in Claim 8 wherein the agent is a fluorination agent comprising a source of fluorine associated with an activating component for example liquid phase HF and a carrier.

11. Process as claimed in any of Claims 1 to 10 for the preparation of pharmaceutical, veterinary product, agrochemical and polymeric compounds and libraries of such compounds, and their synthetic intermediates.

12. Process as claimed in any of Claims 1-11 wherein a compound of formula II is obtained from compounds of formula III:

(III) 

And a compound of formula III as hereinbefore defined is obtained by reaction of a compound of formula IV:

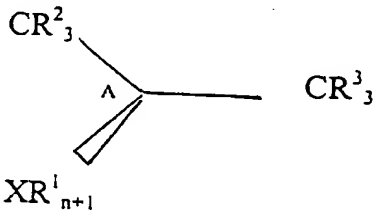
(IV) 

with a compound of formula V:

(V) R^2MgBr.

13. Novel intermediate of the formula II, III, IV, or V as defined in Claim 12.

14. Process as claimed in any of claims 1 to 13 comprising in an additional stage the modification or interconversion of a compound of formula I to a compound of the formula Iii:

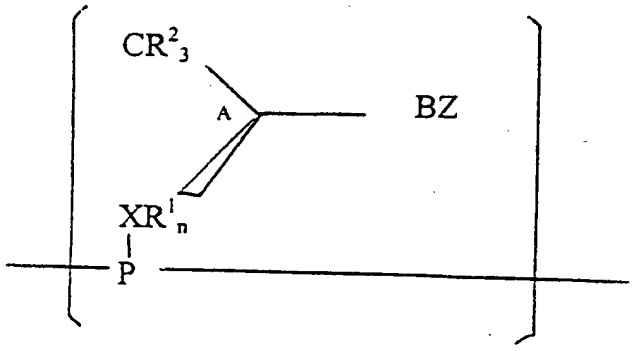
(Iii) 

by the functional modification of a compound of formula I as hereinbefore defined to include additional groups R^1 and R^3 or the interconversion of a compound of formula I as hereinbefore defined.

15. Compound of the formula I as hereinbefore defined in any of Claims 1 to 7 wherein A, B, Z and R^1 are as hereinbefore defined, X is N and n is 1 with the exception that R^2 is not phenyl or benzyl when R^1 is hydrogen, BH is phenyl or CH_3 and Z is H.

16. Process for the preparation of enantiomerically pure chiral polymer comprising a repeating unit of the formula Ii:

(Ii)



wherein P is derived from a polymerisable monomer or oligomer and X, R^1, R^2, B, Z and A are as hereinbefore defined;

comprising coupling a compound of formula I as hereinbefore defined with a monomer or oligomer and subsequently polymerising.

17. Process as claimed in Claim 16 wherein a polymerisable monomer is selected from the group consisting of: an epoxy resin; an addition-polymerisation resin; a formaldehyde condensate resin; a cyanate resin; and an isocyanate resin; polyaromatics; monomers of natural polymers including carbohydrates, polypeptides and proteins including starch, celluloses, collagen, gelatin, dextrans, alginates, chitin and chitosan; and monomers of

biodegradeable and/or biocompatible polymers including poly(lactic acid), poly(glycolic acid), polycaprolactone, polyorthoesters, polyanhydrides, polyaminoacids and azo polymers; and mixtures thereof.

18. Polymer as defined in Claim 17.

19. Polymer as defined in Claim 17 as a delivery agent for a pharmaceutical, veterinary product or agrochemical *in situ*.

20. Use of one or more compounds of formula I as hereinbefore defined in the preparation of a library of compounds.

21. Process for the preparation of a library of compounds of formula I as hereinbefore defined comprising:

reacting one or more compounds of formula IV as hereinbefore defined with a plurality of compounds of formula V as hereinbefore defined, and converting via compounds of formula II as hereinbefore defined to compounds of formula I as hereinbefore defined; and

optionally labelling the support or vessel with means to identify the synthetic history of the supported or contained compound.

22. Library of compounds of formula I, II or III as hereinbefore defined.

23. Pharmaceutical, veterinary product or agrochemical composition comprising a compound of formula I, Ii or Iii as hereinbefore defined with suitable diluents, adjuvants, carriers and the like.